

PRODUCTION OF ZINC OXIDE**Publication number:** JP2001039713 (A)**Publication date:** 2001-02-13**Inventor(s):** KOBAYASHI KENJI; KANO KOJI**Applicant(s):** NIPPON TELEGRAPH & TELEPHONE**Classification:****- International:** C03B8/02; C01G9/02; C03B8/02; C01G9/00; (IPC1-7): C01G9/02; C03B8/02**- European:****Application number:** JP19990210145 19990726**Priority number(s):** JP19990210145 19990726**Abstract of JP 2001039713 (A)**

PROBLEM TO BE SOLVED: To produce high purity zinc oxide by preparing a zinc carbonate precipitate by dissolving high purity zinc in an acid soln. and adding sodium carbonate, or the like, and dehydrating, drying and burning the precipitate. **SOLUTION:** The high purity zinc low in transition metal impurities such as Fe, Ni and Cu and having $\geq 99.999\%$ purity is used as a starting material, and the high purity zinc is dissolved in an acid soln. such as hydrochloric acid, nitric acid and sulfuric acid, and high purity acid having $\geq 99.99\%$ purity is used. Then, the high purity sodium carbonate or sodium bicarbonate having $\geq 99.99\%$ purity is added to the zinc soln. after being dissolved to precipitate the zinc carbonate precipitate. The high purity zinc oxide very low in transition metal impurities is obtained by washing the precipitate by adding ultrapure water to the precipitate and agitating the mixture, then dehydrating the precipitate by suction filtration or centrifugal separation, drying it by vacuum drying or in an oxygen atmosphere and burning the dried product in an electric furnace at ≥ 300 deg.C, preferably at 400-600 deg.C.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]**[0001]**

[Field of the Invention]This invention relates to the manufacturing method of the zinc oxide of a high grade, and more particularly the manufacturing method of the high grade oxide material for light amplifiers.

[0002]

[Description of the Prior Art]A zinc oxide (ZnO) is one of the tellurite glasses or composition raw materials of tellurite glass fiber which use as the main ingredients the tellurium dioxide which becomes a basis of an optical amplification medium, and the light amplifier and laser device which used this.

[0003]About the manufacturing method of the conventional zinc oxide, on the method and concrete target which get carbon dioxide in an operation of the saturated sodium bicarbonate solution in the solution of zincic acid, a potassium bicarbonate solution is added to the solution of the sulfate of zinc of zinc salt, and it calcinates and manufactures at an elevated temperature after producing zinc carbonate.

[0004]In a conventional method, use the solution of zinc salt like sulfate of zinc, and the solution of zincic acid as a starting material, and in this solution still more specifically Namely, sodium carbonate, Or the solution of sodium bicarbonate is added, respectively, it calcinates at an elevated temperature after producing basic zinc carbonate and neutral zinc carbonate, and a zinc oxide is obtained.

[0005]About the manufacturing method of the conventional zinc oxide, the solution of zinc salt or zincic acid is used as a starting material. Since the zinc solution of a high grade is not being used for the solution of zinc salt or zincic acid, the point that the thing of the high grade is not obtained about the manufactured zinc oxide, either is a fault. In a conventional method, in order to remain as an impurity into the zinc oxide which the trace of sulfuric acid of the used sulfate of zinc manufactured and to remove this, it heats above 800 ** and there is complicatedness which must be used as the zinc oxide

except the trace of sulfuric acid.

[0006]

[Problem(s) to be Solved by the Invention]The purpose of this invention by using the metal zinc of the high grade which removed the impurity of transition metals, such as Fe, Cu, and nickel, for a starting material, It is in providing the method of manufacturing the zinc oxide of the high grade which solved the fault of manufacture of a zinc oxide with low purity which uses solution with many impurities, such as zinc salt or zincic acid, as a starting material.

[0007]

[Means for Solving the Problem]In order to solve an aforementioned problem, a manufacturing method of a zinc oxide by this invention, High purity zinc is used as a starting material, said high purity zinc is dissolved in an acid solution, sodium carbonate or sodium bicarbonate is added to a zinc solution after the dissolution, a sediment of zinc carbonate is produced, and this sediment is dried and dried and is calcinated.

[0008]High-purity-metal zinc about high-purity-metal zinc of any shape Namely, chloride, After making it dissolve within acid solutions, such as nitric acid and sulfuric acid, sodium carbonate or sodium bicarbonate is added in solution after the dissolution, a sediment of zinc carbonate is produced, this sediment is dried and dried, it is considered as zinc carbonate, this is calcinated above 300 more **, and it is considered as a zinc oxide of a high grade.

[0009]In order that this invention may solve problems, such as a method of adding sodium carbonate or a sodium bicarbonate solution to zincic acid of conventional technology, or solution of zinc salt, and manufacturing a zinc oxide from basic or neutral zinc carbonate, Purity with few transition metal impurities, such as Fe, nickel, and Cu, about metal zinc of not less than 99.999% of high grade. It does not restrict powdered, but metal zinc of all shape of the shape of a shot and the shape of an ingot is used for a starting material, and they are a zinc oxide with few transition metal impurities, and a thing which manufactures a zinc oxide of a high grade especially.

[0010]

[Embodiment of the Invention]Hereafter, this invention is explained concretely. The zinc of a high grade is useful on a use among the metal zinc used as a starting material in this invention. As for the grade of a high grade, not less than 99.999% (i.e., more than 5N) is preferred. It is not restricted to the shape of metal zinc. That is, powder, the shape of an ingot, and the shape of a shot-like throat may be sufficient.

[0011]In this invention, the above high purity zinc is dissolved with acid. The dissolutions by acid should just be the conditions which do not need special conditions but can dissolve this metal zinc into acid solutions, such as chloride, nitric acid, and sulfuric acid. Special conditions are not needed about the heating and dissolving of the solution which dissolved this metal zinc. As said acid, chloride, nitric acid, sulfuric acid,

etc. can be used as mentioned above, and not less than 99.99% of the purity is desirable in order to manufacture a high grade zinc oxide.

[0012]Next, it settles [add sodium carbonate or sodium bicarbonate to this zinc solution, and] zinc carbonate and dries [wash and]. In order for such sodium carbonate or sodium bicarbonate to also manufacture a high grade zinc oxide, it is preferred that purity is not less than 99.99%.

[0013]What is necessary is just to wash, while washing operation of the hydrate of zinc carbonate also adds and stirs ultrapure water, and the method in ordinary use may be used also for drying, and suction filtration or a centrifuge is preferred for it operationally. The method of desiccation and the daily use also about calcination may be used, and vacuum drying or the desiccation by oxygen environment, and the calcination in the electric furnace in oxygen environment are suitable for the last operationally. As for calcination temperature, it is good that it is not less than 300 **. It is because there is a possibility that CO₂ may not diffuse enough that it is less than 300 **. Although the maximum of calcination temperature is not limited, there are many losses of energy that it is an elevated temperature not much, and it becomes fundamentally efficient less. It is 400-600 ** especially preferably.

[0014]As mentioned above, as explained concretely, in the case of the method of manufacturing the zinc oxide of a high grade especially, in this invention method. Use the zinc salt or zincic acid of conventional technology as a starting material, dissolve in acid, and sodium carbonate or sodium bicarbonate is added, The method of considering it as zinc carbonate, calcinating this at an elevated temperature, and using as a zinc oxide uses high-purity-metal zinc as a starting material, and differs in that sodium carbonate or sodium bicarbonate of a point and a high grade which dissolves in acid of a high grade is added.

[0015]

[Example]Hereafter, although an example explains this invention still more concretely, this invention is not limited to these examples.

[0016]

[Example 1] Purity: Process drawing shown in drawing 1 explains the manufacturing method of the high grade zinc oxide which uses the high-purity-metal zinc of 7N (99.99999%) as a starting material. Shape carries out weighing of the shot-like high purity zinc 50g, and it puts into a 1000-ml beaker, and dissolves in 300 ml of concentrated hydrochloric acid (36% of hydrogen chloride content) of the high grade for electronic industry. In about 30 minutes, the solution after the dissolution is colorless, and the time which the dissolution takes removes undissolved zinc with a membrane filter, when there is zinc which is not dissolved [through and] about a membrane filter with the aperture of 0.2 micro in a colorless solution. In this solution, 100 g of high grade

sodium carbonate (Na_2CO_3) whose purity is 99.99% is added every in small quantities, and a ZnCO_3 sediment is obtained in it. This sediment separates a sediment and solution with a centrifuge. The sediment after separation is put into a 1000-ml beaker, and washes by adding 800 ml of ultrapure water again. Washing operation is repeated 3 times. With a centrifuge, separate the ZnCO_3 sediment after washing and the ZnCO_3 sediment after separation, It dries by drying at 100 °C by a vacuum dryer for 24 hours, calcinates in 400 °C after manufacturing the zinc carbonate (ZnCO_3) of a high grade within the electric furnace of pure oxygen environment, and is considered as a zinc oxide. The reaction formula can manufacture a high grade zinc oxide at the reaction of the formula 1, the formula 2, and the formula 3.

[0017]

[Formula 1] $\text{Zn} + 4\text{HCl} \rightarrow \text{ZnCl}_4^{2-} + 2\text{H}_2$ [0018]

[Formula 2] $\text{ZnCl}_4^{2-} + \text{Na}_2\text{CO}_3 \rightarrow \text{ZnCO}_3 + 2\text{NaCl} + \text{Cl}_2$ [0019]

[Formula 3] $\text{ZnCO}_3 \rightarrow \text{ZnO} + \text{CO}_2$ [0020] Drawing 2 is a TG (thermogravimetric analysis)-

DTA (differential thermal analysis) curve of the zinc carbonate after vacuum drying. In drawing 2, (%) and the rate of weight loss, and a right longitudinal axis **** calorific capacity (microvolt) in DTA. [in / a horizontal axis can be set to temperature (°C) and / in a left-vertical axis / TG] From drawing 2, carbon dioxide was emitted 150 °C - near 300 °C from zinc carbonate, and the endothermic peak used as a zinc oxide (ZnO) was observed from it. That is, the substance produced from the analysis result in an X diffraction (XRD) and thermometric analysis (TG-DTA) is anhydrous zinc carbonate (ZnCO_3).

[0021] Activation analysis of Fe of the produced anhydrous zinc carbonate (ZnCO_3), nickel, and Cu is conducted, Each element has produced the anhydrous zinc oxide of the high grade of triple or more figures about Fe, nickel, and Cu rather than the fixed-quantity value of the impurity concentration of Fe about the zinc oxide in which an analysis result of 1 ppb or less was obtained, and impurity concentration was manufactured conventionally, nickel, and Cu. The yield of the anhydrous zinc oxide of the high grade in this example is 90%.

[0022] Use as an accessory constituent the zinc oxide (ZnO) produced by this example, and to this. the tellurite glass fiber (core glass presentation: -- TeO_2 -ZnO- Na_2O - Bi_2O_3 --) which added the tellurium dioxide (TeO_2) of the main ingredients, Na_2O of other accessory constituents, and Bi_2O_3 [3 and] Clad glass composition: When the single mode fiber of TeO_2 -ZnO- Na_2O was produced, wavelength has produced the with a loss value of 10dB/km fiber in 1.3 micro. Conventionally, since the tellurite glass fiber of

elegance used the commercial ZnO raw material, this has attained reduction of the large loss value to the loss value at 1.3 micro having shown the value high in km and 1000dB /.

[0023]

[Example 2] Purity: Process drawing shown in drawing 3 explains the manufacturing method of the high grade zinc oxide which uses the high-purity-metal zinc of 6N (99.9999%) as a starting material. Shape carries out weighing of the ingot-like high-purity-metal zinc 25g, and it puts into a 1000-ml beaker, and dissolves in the aqua fortis which added 200 ml of ultrapure water to 300 ml of concentrated nitric acid (61%, specific gravity = 1.42g/cm³) of the high grade for electronic industry. The time which the dissolution takes is about 1 hour. The solution after the dissolution is colorless, and when there is metal zinc which is not dissolved [through and] about a membrane filter with the aperture of 0.2 micro, it removes a colorless solution with a MEMPURAN filter. In this solution after the dissolution, 100 g of high grade sodium carbonate (Na₂CO₃) whose purity is 99.99% is added every in small quantities, and a ZnCO₃ sediment is obtained in it. This sediment separates a sediment and solution with a centrifuge. The sediment after separation is put into a 1000-ml beaker, and washes by adding 800 ml of ultrapure water again. Washing operation is repeated 3 times. With a centrifuge, separate the ZnCO₃ sediment after washing and the ZnCO₃ sediment after separation, It dries by drying in 170 ** for 24 hours by a vacuum dryer, calcinates at 600 ** within the electric furnace of pure oxygen environment after manufacturing the zinc carbonate (ZnCO₃) of a high grade, and is considered as a zinc oxide.

[0024]The reaction formula can manufacture zinc carbonate according to the formula 4 and the formula 5. If zinc carbonate is calcinated at 600 **, according to the formula 6, a zinc oxide is producible. The substance which the same thing as the DTA curve shown in drawing 2 also in the DTA curve by TG-DTA analysis was obtained, and was produced from the analysis result in an X diffraction (XRD) and thermometric analysis (TG-DTA) is a zinc oxide. Conduct activation analysis of Fe of the produced zinc oxide, nickel, and Cu, and an analysis result with an impurity concentration of 1 ppb is obtained about Fe, nickel, and Cu, Conventionally, the anhydrous zinc oxide of the high grade of triple or more figures has produced with the yield of 95% rather than the fixed-quantity value of Fe about the zinc oxide currently performed, nickel, and Cu impurity concentration.

[0025]

[Formula 4] $\text{Zn} + 2\text{HNO}_3 \rightarrow \text{Zn}^{2+} + 2\text{NO}_3^-$ [0026]

[Formula 5] $\text{Zn}^{2+} + \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} \rightarrow \text{ZnCO}_3 + 2\text{NaOH}$ [0027]

[Formula 6] $\text{ZnCO}_3 \rightarrow \text{ZnO} + \text{CO}_2$ [0028] the tellurite glass fiber (core glass presentation: $\text{--TeO}_2\text{--ZnO--Na}_2\text{O--Bi}_2\text{O--}$) which added TeO_2 to this using ZnO produced by this example [3 and] Clad glass composition: In $\text{TeO}_2\text{--ZnO--Na}_2\text{O}$, the with a loss value of 10dB/km single mode fiber has been produced on the wavelength of 1.3 micro. This has attained reduction of the large loss value to the single mode fiber which the conventional tellurite fiber raw material produced using the raw material of commercial ZnO to TeO_2 being a loss value of 1000dB/km.

[0029]

[Example 3] Purity: Process drawing shown in drawing 4 explains the manufacturing method of the high grade zinc oxide which uses the metal zinc of the high grade of 6N (99.9999%) as a starting material. Shape carries out weighing of the chunk-like high-purity-metal zinc 50g, and it puts into a 1000-ml beaker, and dissolves in the dilute-sulfuric-acid solution which added 200 ml of ultrapure water to 300 ml of concentrated sulfuric acid (96%) of the high grade for electronic industry. The sediment of white sulfate of zinc is obtained simultaneously with the dissolution. The sediment of sulfate of zinc is heated on a hot plate, and it dissolves. The zinc solution after the dissolution is colorless, adds a little solution which dissolved 100 g of high grade sodium carbonate (Na_2CO_3) whose purity is 99.99% in 300-ml ultrapure water every in this solution after the dissolution, and obtains a ZnCO_3 sediment in it. This sediment separates a sediment and solution with a centrifuge. The sediment after separation is put into a 1000-ml peaker, and washes by adding 800 ml of ultrapure water again. Washing operation is repeated 3 times. With a **** eliminator, separate the ZnCO_3 sediment after washing and the ZnCO_3 sediment after separation, It dries by drying at 130 ** by a vacuum dryer for 24 hours, calcinates at 600 ** within the electric furnace of pure oxygen environment after manufacturing the zinc carbonate (ZnCO_3) of a high grade, and is considered as a zinc oxide.

[0030] The reaction formula can manufacture a zinc oxide according to the formula 7, the formula 8, the formula 9, and the formula 10.

[0031]

[Formula 7] $\text{Zn} + \text{H}_2\text{SO}_4 \rightarrow \text{ZnSO}_4 + \text{H}_2$ [0032]

[Formula 8] $\text{ZnSO}_4 \rightarrow \text{Zn}^{2+} + \text{SO}_4^{2-}$ [0033]

[Formula 9] $\text{Zn}^{2+} + \text{CO}_3^{2-} \rightarrow \text{ZnCO}_3$ [0034]

[Formula 10] $\text{ZnCO}_3 \rightarrow \text{ZnO} + \text{CO}_2$ [0035] What has TG-DTA analysis the same as that of the curve shown in drawing 2 is obtained. That is, the substance produced from the analysis result in an X diffraction (XRD) and thermometric analysis (TG-DTA) is an

anhydrous zinc oxide. Activation analysis of Fe of the produced anhydrous zinc oxide, nickel, and Cu is conducted, The analysis result whose impurity concentration is 1 ppb was obtained about Fe, nickel, and Cu, and the anhydrous zinc oxide of the high grade has produced with the yield of 95% in about triple figures conventionally rather than the fixed-quantity value of Fe about the zinc oxide currently performed, nickel, and Cu impurity concentration.

[0036]the tellurite glass fiber (core glass presentation: -- TeO_2 - ZnO - Na_2O - Bi_2O_3 --) which added TeO_2 as main composition to ZnO produced by this example [3 and] Clad glass composition : The place which produced the single mode fiber by TeO_2 - ZnO - Na_2O , Since the loss value with a wavelength of 1.3 micro of 10dB/km was acquired and the conventional tellurite glass raw material used the raw material of the marketing ZnO , in 1.3 micro, reduction of the large loss value was completed to only the loss value of 1000dB/km having been acquired.

[0037]

[Effect of the Invention]As explained above, according to the manufacturing method of this invention, the metal zinc of a high grade is used as a starting material, sodium carbonate or sodium bicarbonate is added after dissolving in acid of a high grade, and if it calcinates, the zinc oxide of an anhydrous high grade is producible after [after producing the sediment of zinc carbonate] drying / desiccation. It compares with the method of obtaining carbon dioxide in an operation of the saturated sodium bicarbonate solution or a sodium carbonate solution in conventional zincic acid or the solution of zinc salt especially, Since an anhydrous zinc oxide is produced very simple, the zinc oxide of the high grade which made the transition metal super-low concentration can be manufactured. There is an advantage which can manufacture an optical fiber amplifier with high amplification by using a zinc oxide as a starting material of the light amplifier using tellurite glass fiber.

[Translation done.]

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CLAIMS

[Claim(s)]

[Claim 1]A manufacturing method of a zinc oxide high purity zinc is used as a starting material, and said high purity zinc is dissolved in an acid solution, adding sodium carbonate or sodium bicarbonate to a zinc solution after the dissolution, producing a sediment of zinc carbonate, drying and drying this sediment and calcinating it.

[Claim 2]A manufacturing method of the zinc oxide according to claim 1 in which high purity zinc is high purity metal of not less than 99.999% of purity, purity is a reagent of not less than 99.99% of high grade, and sodium carbonate or sodium bicarbonate is also characterized by purity being a reagent of not less than 99.99% of high grade also about acid.

[Claim 3]A manufacturing method of the zinc oxide according to claim 1 or 2, wherein said calcination temperature is not less than 300 **.

[Translation done.]